

# THE EFFECT OF SHORT REACTION TIME ON THE LIQUEFACTION OF AN AUSTRALIAN BROWN COAL

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## INTRODUCTION

Short Reaction Time (SRT) liquefaction has attracted much research in recent years (1-11). The process, which involves dissolution of coal in a donor solvent during a short time domain, has many advantages over conventional longer reaction time systems. These include the consumption of negligible gaseous hydrogen, utilizing instead the inherent hydrogen in the coal via shuttling and aromatic transfer mechanisms (1,2). The design and mathematical modelling of continuous reactors is also facilitated by the knowledge of the behaviour of the coal at short residence times. The rapidity of the process has led to the development of two-stage liquefaction systems based on this new technology, thus enabling the decoupling of thermal from catalytic processes. Preliminary research on SRT systems has shown their potential to give significantly lower gas and higher liquid yields, hence enabling more efficient utilization of hydrogen in the liquefaction process.

The majority of the research has involved US bituminous coals, with Whitehurst (3) reporting that optimum oil yields are achieved with coals in the 77-87% CMAF range. He postulated the observed lower yields for the lower rank coals were a consequence of the insolubility of the initially formed fragments in the donor solvent due to their more polar nature. Other workers (12) have suggested the lack of rapid dissolution is a function of these coals having more alicyclic, rather than hydroaromatic and aromatic systems, and hence are less capable of internal hydrogen donation.

The liquefaction of an Australian bituminous coal, Liddell, at SRT conditions has recently been reported (9,10,11). The authors observed trends similar to those found for US bituminous coals, with significant conversion occurring within the first few minutes of reaction. To determine whether Australian low rank coals display similar SRT behaviour to their US counterparts a Victorian brown coal has been investigated. This paper reports the results of the study; emphasizing conversion, oil yields and product analyses.

The coal used for this study was a medium-light lithotype Victorian brown coal from the Loy Yang Field (bore 1277, depth 67-68 m). The dried coal (particle size range: 90-150  $\mu\text{m}$ ) was injected into the donor solvent, tetralin, at temperature. The SRT reactor and details of its operation are described elsewhere (10,11). The reaction temperature was 380°C, the solvent to coal ratio 6:1, and the hydrogen pressure after injection typically 2100-2350 psig. The reaction times investigated were: 0, 2, 3, 4, 10, 20, 45 and 120 minutes.

The Total Oils (defined as  $\text{CH}_2\text{Cl}_2$  solubles) and residues have been investigated and characterized by a variety of analytical and spectroscopic methods. This has enabled both physical and chemical insights into the reactions occurring during the initial and subsequent dissolution of the brown coal.

## RESULTS AND DISCUSSION

The product distribution data (Table 1) shows both the conversion and oil yields to increase with reaction time. Surprisingly, there is conversion at zero time, which is associated mainly with gas production as reflected in the very high gas/oil yield ratio. Gas analyses however show its composition to be overwhelmingly carbon oxides with only a minor portion of hydrocarbon gases. Similar gas compositions are observed at the other reaction times with only the absolute amounts of the gases varying. The general trend is to increasing gas yields with reaction time. Although  $\text{CO}_2$  and CO dominate the gas production at all reaction times, the hydrocarbon gases do not become significant until 20 minutes of reaction time. Prior to this they are only in trace amounts. The zero time conversion suggests that contact of the dried coal with the hot solvent for only a few seconds is sufficient to promote decarboxylation,

decarbonylation and to a much lesser extent dealkylation reactions. The oil yield at zero time may possibly arise from the easily extractable, non-covalently bonded material in the coal matrix as 3.47% of the coal is solvent extractable (14). Decomposition and dissolution of the coal structure is significant even at 3 minutes with conversions of greater than 20%.

The data indicate the existence of two distinct reaction time zones; the first being prior to 10 minutes and the second from this time. In the first few minutes of reaction there is much gasification as defunctionalization reactions of the coal matrix occur. This is markedly illustrated by both the gas yields and gas/oil yield ratios. The amount of water production is relatively constant indicating the major reaction processes are rupture of the weaker bonds in the coal structure rather than dehydroxylation and upgrading of solubilized species. However, in the second time zone gas production remains constant, with the gas/oil yield ratio actually decreasing, suggesting that gasification is now mainly dependent on the removal of alkyl substituents rather than carboxyl and carbonyl functional groups. These have been predominantly removed within the first few minutes of reaction. The water yield increases significantly as does the  $H_2O$ /oil yield ratio indicating the removal of hydroxyl moieties. These may arise either from dehydroxylation of the coal matrix to aid its dissolution or from the upgrading of the already solubilized fragments.

Donor solvent hydrogen consumption data also supports the concept of two separate reaction periods. As expected, little hydrogen is consumed during the initial stages of dissolution, where the removal of carboxyl and carbonyl groups, via gasification, is dominant. This low hydrogen consumption may be a direct result of the coal utilizing its inherent hydrogen by shuttling type mechanisms. Although consumption does increase with time, it is much greater during the latter reaction period. The hydrogen is required to stabilize radical species produced by both cleavage and more vigorous defunctionalization of the coal matrix.

The conversion value for 120 minutes is very similar to that reported (15) for the same coal hydrogenated under conventional batch autoclave conditions (56% cf. 60%), although the oil yields differ markedly (25% cf. 46%). This difference is difficult to rationalize and results from the much higher water and gas yields for the SRT experiment. The Loy Yang conversions and oil yields are lower than those reported for Liddell coal under similar conditions. The parallel between increasing water production and oil yield tends to give credence to Whitehurst's hypothesis that the lower oil yields at short times for low rank coals are due to the insolubility of the very polar initially formed fragments.

The elemental analyses of the residues (Table 2) shows increasing carbon and decreasing oxygen contents with increasing reaction time. The removal of heteroatom moieties is further evidenced by the O/C ratios which similarly decrease. The H/C ratios however decrease only slightly with time suggesting the difficulty of dealkylation reactions and hence the relative preservation of hydrogen in the residues. The similar H/C values for the various reaction times indicate the residues are mainly the result of loss of peripheral heteroatom functionalities and not subject to gross structural alteration such as forming polycondensed aromatic systems. If this were the case it would be reflected in a significant lowering of H/C values with time. The H/C ratio for the zero time residue is lower than for the parent coal confirming the instantaneous gasification and extraction of non-bound material. The general trends in the Total Oils are also decreasing oxygen and increasing carbon contents with time. This correlates with increasing H/C and decreasing O/C ratios, showing a loss of heteroatom functionality and a lowering of the condensed nature (16) of the oils with time. Again the data can be divided into two regions centered on 10 minutes, as demonstrated by the much lower H/C and O/C ratios after this time compared to those prior. This further implies the time dependency of different liquefaction processes.

The IR Spectra (Fig. 1) of the residues both qualitatively and semiquantitatively support the forementioned data. The hydroxyl absorption decreases only marginally in the first few minutes of reaction but more markedly at longer times. This corresponds with the observed water yields. Similarly the carbonyl

absorption decreases rapidly with time and correlates with the production of carbon oxides. Whitehurst (3) has observed for low rank coals a good correlation between the loss of oxygen and the formation of carbon dioxide and carbon monoxide. There is also proportionate increases in aromatic C=C stretching and C-H bending with time, suggesting the residues are acquiring greater aromatic character. The proportion of aliphatic C-H stretching and bending vibrations slightly increase with time paralleling the loss of heteroatom functionality. This further illustrates the relative inertness of alkyl compared to heteroatom functionalities, and supports the forementioned gas composition data.

The trends are not as well defined for the Total Oil (TO) (Fig. 2), with the hydroxyl absorptions although being proportionately larger (approx. 16%) varying little with time. This implies that the forementioned increased water production is more likely a result of cleavage and dissolution of the matrix rather than upgrading of the already solubilized species. There is a general decrease in the carbonyl absorptions with time, while the converse is observed for the aliphatic C-H stretchings. The aromatic C-H bending, although a large percentage at 2 minutes (approx. 15%) decreases rapidly to a constant value (approx. 8%) from 4 minutes onwards. This is generally at the expense of increasing aromatic C=C and aliphatic C-H stretchings.

CP-MAS  $^{13}\text{C}$  nmr of the residues (Fig. 3) further illustrates the significant reactivity of the coal at SRT. The aromaticity,  $f(a)$ , increases dramatically after only 2 minutes reaction from 0.61 in the parent coal to 0.78 in the residue. Even at zero time  $f(a)$  is 0.63, reflecting the loss of carboxyl and carbonyl groups as gases. The  $f(a)$  values increase only marginally from 0.78 to 0.83 with time, supporting earlier conclusions from elemental analyses that all the residues have similar aromatic structure, differing mainly in degree of functionality.

$^1\text{H}$  nmr and structural parameters derived from Brown-Ladner equations (Table 3) give additional information on the nature of the TO. The percentage of exchangeable protons  $[H(\text{exch})]$  increases with time, showing an increasing proportion of phenolic groups in the oils. This trend was not as evident from IR data. The values for  $H(\text{exch})$  further suggest two reaction time zones as they cluster into two discrete groups. Although there are no discernable trends with the percentage of aromatic protons ( $H_{ar}$ ), the percentage of protons on carbons  $\beta$  and further from aromatic rings ( $H_0$ ) tend to increase with time. This is also shown in the values for the average chain length ( $n$ ). The oil produced at zero time has both the greatest proportion of  $H_0$  and the largest value of  $n$ , suggesting it is only the solvent extractable material from the coal. Solvent extracts of a Victorian brown coal of the same lithotype have been observed to contain a significant amount of straight chain material, either as alkanes, alcohols or fatty acids (17). The value of  $n$  then decreases to a minimum at 10 minutes and increases to 120 minutes; indicating more complete decomposition of the coal in this longer time domain. The increased chain lengths could result from cleavage of alicyclic systems. The aromaticity,  $f(a)$ , and degree of aromatic substitution,  $\sigma$ , generally decrease with increasing reaction time. The trends for the parameter  $\frac{H_{ar}}{C_{ar}}$ , i.e., the degree of condensation, are not as clearly defined, but it appears to increase with time implying smaller size aromatic systems. The decrease in aromaticity and substitution of the oil implies that either some upgrading of the initially solubilized material has occurred or the later dissolved material was more defunctionalized prior to dissolution. More likely it is a combination of both processes.

The Molecular Weights (MW) of the Total Oil (Table 3) are all similar with the number average MW ( $M_n$ ) varying from 210-320 with no readily identifiable trend with time. The values of  $M_n$  are low compared to that reported for an oil produced from the same coal under normal batch autoclave conditions ( $M_n = 487$ ). The weight average MW ( $M_w$ ) and MW distribution (MWD) also show no apparent trends. These observations are most likely a direct consequence of the insolubility of a large portion of the oils in the solvent, THF, used for MW determination. Hence only smaller MW species from the very heterogeneous Total Oil have been selectively dissolved. This insolubility may be itself indicative of the high MW of these Total Oils.

Pyrolysis-Gas Chromatography of the residues (Fig. 4) reveals a major

reduction of aliphatic components within the first 4 minutes of reaction, and with only alkyl phenols and catechols remaining after 45 minutes. This indicates that the more easily accessible and removable aliphatic material is extracted preferentially from the coal matrix in the initial stages of dissolution, while at longer times the coal structure itself must be more severely decomposed to increase the oil yield. This is also revealed by the decrease in the percentage of residue pyrolysed. The presence of phenolic species is directly relatable to the lignin input to the brown coal. Their existence in the pyrograms of the residues from 20 and 45 minutes supports the hypothesis that further oil production results from cracking of the lignin-type components of the coal macromolecules. Pyrolysis-Gas Chromatograms of the TOs, which are in effect simulated distillation profiles, all appear very similar. They differ quantitatively rather than qualitatively in composition.

The residues were degradatively oxidized by peroxytrifluoroacetic acid, a technique known as Deno Oxidation (18). It selectively oxidizes aromatic rings and leaves the aliphatic portion essentially intact. The data (Table 4) reveals that even at 0 minutes there is a marked reduction in the total yield of aliphatic hydrogen (65.6% cf 54.3%) compared to the parent coal from both assignable and unassignable material. Overall there is a reduction with time for both the total aliphatic and total spectrum hydrogen yields, suggesting the residues are becoming more aromatic in nature. Acetic acid (derived from aryl methyl groups) varies little with time suggesting little increase in dealkylation reactions. Succinic acid (derived from hydroaromatic structures) well illustrates the existence of two reaction zones. It is much reduced in the second due to both a possible internal hydrogen donation and a more severe rupture of the coal structure. Similarly, malonic acid (derived from bridging methylene groups) is also reduced in the second period as a result of bond cleavages and probably accompanying fragmentation of aromatic clusters. The 1° and 2° protons decrease in accord with the total aliphatic hydrogen, whereas the 3° protons vary little with time. However, the protons on carbons  $\alpha$  to carbonyl containing functional groups decrease significantly with time, paralleling the loss of the functional groups as carbon oxides. The data support earlier conclusions from other techniques.

This paper has reported the results of a donor solvent SRT study of a Victorian brown coal. Although oil yields and conversion are lower than for bituminous coals they show trends similar to those reported for USA low rank coals. The dissolution process appears to occur in two chemically and physically distinct phases. One primarily involves extraction of the coal and removal of carboxyl and carbonyl groups while the other involves a more severe disruption and decomposition of the coal matrix and removal of hydroxyl moieties. In both phases dealkylation is not a dominant reaction.

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TABLE 1: PRODUCT DISTRIBUTION

Reaction Time (min)	Conversion %	Oil <sup>A</sup> yield	H <sub>2</sub> O <sup>A</sup> yield	Residue <sup>A</sup>	Gas <sup>A,B</sup>	H <sub>2</sub> O/oil yield	Gas/oil yield
0	9.0	0.90	2.59	91.00	5.50	2.88	6.12
2	12.61	5.12	2.04	87.39	5.45	0.40	1.06
3	21.02	6.08	2.43	78.98	12.51	0.40	2.06
4	27.53	7.63	2.89	72.47	17.01	0.38	2.23
10	32.39	10.65	4.77	67.61	16.91	0.45	1.59
20	39.91	18.08	7.17	60.09	14.66	0.40	0.81
45	48.95	19.55	15.32	51.05	14.08	0.78	0.72
120	56.28	25.92	15.96	43.72	14.40	0.62	0.56

A - g/100 g DAF Coal      B - By difference

TABLE 2: ELEMENTAL ANALYSES

Time (min)	C	H	O <sup>A</sup>	N	H/C	O/C <sup>A</sup>	N/C	Ash
LY 1277	62.35	5.20	31.89	0.59	1.00	0.38	0.01	0.71
Total Oils								
0	74.69	2.48	22.30	0.53	0.40	0.22	0.01	6.00
2	76.43	3.50	19.74	0.33	0.55	0.19	0.00	0.90
3	76.87	4.18	24.50	0.49	0.65	0.24	0.01	2.0
4	68.30	3.77	27.50	0.40	0.66	0.30	0.01	1.0
10	73.84	4.17	21.81	0.16	0.68	0.22	0.00	0.70
20	84.55	5.96	9.14	0.35	0.85	0.08	0.00	0.40
45	82.93	5.87	10.72	0.41	0.85	0.09	0.00	2.40
120	86.98	6.23	6.20	0.50	0.86	0.05	0.00	0.40
Residues								
0	65.24	4.68	29.44	0.65	0.86	0.34	0.01	0.79
2	67.28	4.62	27.39	0.71	0.82	0.31	0.01	0.12
3	68.86	4.62	25.78	0.73	0.81	0.28	0.01	1.13
4	69.35	4.62	25.29	0.74	0.80	0.27	0.01	1.06
10	70.51	4.70	24.06	0.79	0.80	0.26	0.01	1.06
20	72.16	4.70	22.37	0.83	0.78	0.23	0.01	1.06
45	74.40	4.87	19.79	0.95	0.79	0.20	0.01	1.97
120	75.71	5.03	18.23	1.01	0.79	0.18	0.01	2.29

A - Oxygen by difference

TABLE 3: <sup>1</sup>H NMR AND MW DATA ON TOTAL OILS

Time (min)	1H NMR DATA						MW DATA <sup>C</sup>					
	Ho	Ha	Har	H(exch)	Hali Har	Ho Ha n=	f(a) <sup>A</sup>	Haru Car <sup>A</sup>	σ <sup>A</sup>	Mn	Mw	MWD
0	61.9	15.7	22.4	N.D.	3.47	4.96	0.84	0.41	0.74	210	411	1.96
2	28.8	20.1	48.6	1.4	0.95	2.29	0.87	0.59	0.48	260	210	0.81
3	58.3	19.8	24.7	1.8	3.22	3.56	0.67	0.83B	0.61	295	432	1.46
4	31.8	26.6	38.8	1.9	1.51	2.20	0.79	0.88B	0.63	279	331	1.19
10	35.5	29.9	32.1	3.1	2.02	2.18	0.78	0.69	0.59	282	442	1.57
20	47.3	25.4	24.0	3.3	3.03	2.86	0.69	0.57	0.48	319	754	2.36
45	35.7	27.6	32.5	3.7	1.95	2.30	0.73	0.67	0.44	298	304	1.02
120	45.7	20.0	30.5	3.8	2.15	3.28	0.72	0.66	0.35	249	393	1.58

N.D. - Not Determined. A - Brown-Ladner Method. B - High oxygen content in sample.

C - GPC-HPLC method for molecular weight determination

TABLE 4: <sup>1</sup>H NMR SPECTRAL DATA OF (WT %) YIELD OF HYDROGEN APPEARING IN TFA<sup>A</sup> OXIDATION PRODUCTS

Time (min)	1° & 2° Protons (0.3-1.45 ppm)	3° Protons (1.45-2.20 ppm)	Protons α to acids and esters (2.20-3.45 ppm)	Total Aliphatic	Acetic Acid	Succinic Acid	Malonic Acid	Methanol	Total Spectrum	% Oxidized
LY 1277	18.2	17.0	18.4	53.6	6.5	3.8	1.3	0.4	65.6	98
0	11.9	13.1	10.2	35.2	11.0	4.7	2.4	1.0	54.3	93
2	10.1	9.1	9.5	28.7	10.8	3.2	2.0	2.7	47.4	98
3	13.1	11.6	10.0	34.7	14.4	4.5	2.2	2.2	58.0	99
4	13.2	11.0	8.7	32.9	14.0	4.0	2.0	2.2	55.1	98
10	10.1	10.9	9.8	30.8	13.0	4.3	2.3	3.2	53.6	99
20	11.2	11.3	7.1	29.6	12.0	2.7	0.7	3.2	48.2	97
45	9.6	10.5	6.8	26.9	11.7	3.5	1.0	2.9	46.0	98
120	6.5	9.5	5.2	21.2	11.7	3.0	0.8	0.7	37.4	95

A - Peroxytrifluoroacetic acid

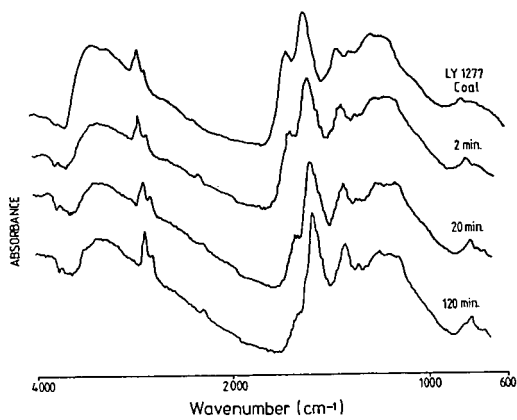


FIG. 1. IR SPECTRA OF LIQUEFACTION RESIDUES

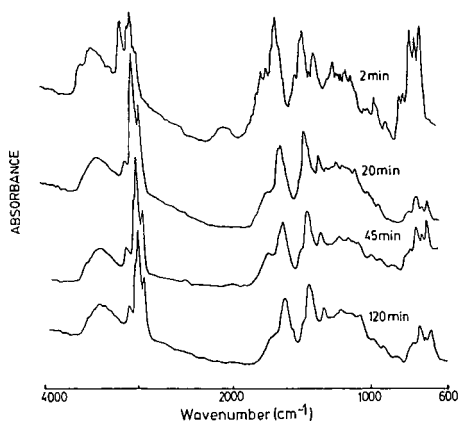


FIG 2. IR SPECTRA OF TOTAL OILS

